

# Colossal enhancement of magnetoresistance in $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ / $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ multilayers: reproducing the phase-separation scenario

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Colossal enhancement of magnetoresistance has been achieved over a broad temperature range which extends upto the room temperature, in ferromagnetic metal-charge ordered insulator manganite multi-layers. The artificially created phase coexistence in the multilayers reproduce the characteristic signatures of metastability in the magnetotransport properties commonly observed in electronically phase-separated manganites.

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There are numerous experimental evidences available now which confirm that transition metal oxides such as manganites are electronically inhomogeneous<sup>1-5</sup>. The length scale of these inhomogeneities or the so called phase separation varies from nanometer up to few microns. Moreover, these inhomogeneities can be manipulated by application of external stimuli such as temperature, magnetic field, etc. Theoretically, however, only nanoscale inhomogeneities have been predicted. It is generally believed that only mesoscale inhomogeneities can give rise to colossal magnetoresistance. Uehara et al.<sup>1</sup> explained the colossal magnetoresistance in a system of coexisting phases such a ferromagnetic metallic (FM) and antiferromagnetic insulator (AFI). The spin alignment among the FM domains are random which becomes aligned on application of magnetic field resulting in gigantic enhancement of conductivity. It was suggested that such mesoscopic phase separation was necessary for colossal responses. Besides this spatially static phase-separation picture, Fath et al.<sup>2</sup> presented an alternative explanation where the increase of FM volume fraction at the cost of AFI domain on application of magnetic field forming a percolation cluster leads to the colossal enhancement of conductivity. Later on, different experimental techniques such as magnetic force microscopy, transmission electron microscopy, photoemission spectroscopy have been employed for probing phase separation<sup>3-5</sup>. Zhang et al.<sup>3</sup> showed that magnetic domains evolve with temperature resulting in magnetic hysteresis which coincides with the hysteresis in resistivity. Loudon et al.<sup>4</sup> suggested that the mesoscopic ferromagnetic region is itself inhomogeneous at the nanoscale with co-existing metallic and charge-ordered regions. Sarma et al.<sup>5</sup> indicated a possible memory effect associated with the electronic inhomogeneities. Apart from the microscopic probes, the electronic phase separation can be detected by studying the macroscopic properties such as transport and magnetization. Very recently, magnetic structure of a series of  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  (LSMO) /  $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  (PCMO) superlattices has been studied, and the possibility of tuning phase separation by imposing appropriate geometrical constraints which favor the accommodation of FM nanoclusters within the “non-FM” material has been emphasized<sup>6</sup>. In this article, we

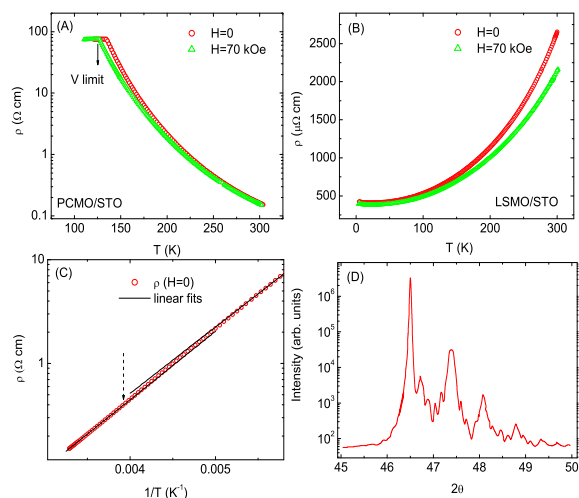


FIG. 1: (Color online) The temperature dependence of resistivity in absence as well as in presence of strong magnetic field for A) PCMO and B) LSMO films. C) Logarithm of resistivity plotted against inverse of temperature for PCMO. The linear fits indicate two different regions. The blown out portion of the transition region is shown where the arrow-head corresponds to  $T_{co}$ . D) A representative x-ray diffraction  $\theta - 2\theta$  scan for one of the multilayers (LSPC3) showing oscillation of the Bragg-peak (002) characteristic of superlattice structures.

will show that if the thickness of the alternate layers in LSMO/PCMO superlattice is properly tuned, it is possible to mimic the characteristic transport and magnetic responses of spontaneously phase separated manganites.

Manganite multilayers are also interesting from the technological point of view since they are capable of exhibiting colossal magnetoresistance. The systems which exhibit large magnetoresistance (MR) are technologically useful for application as magnetic field sensors and memory devices. Microfabricated devices such as magnetic tunnel junctions<sup>7,8</sup> do exhibit large MR. However, the sample fabrication is extremely difficult, costly and time-consuming. Moreover, there are other serious issues such as the sharp bias dependence of tunnel magnetoresistance

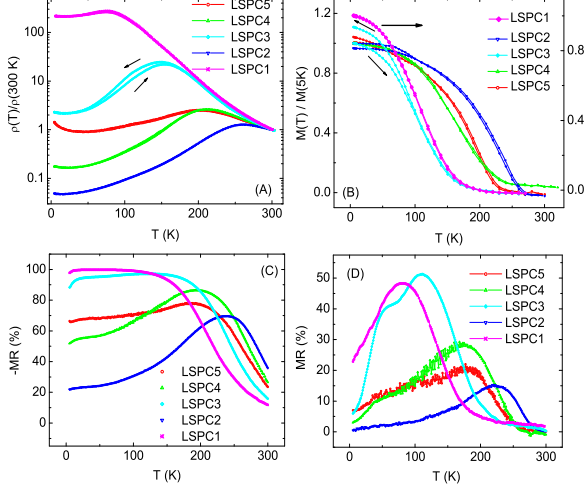


FIG. 2: (Color online) A: The temperature dependence of zero-field cooled resistivity during the cooling and warming cycle for all the samples. B: Field cooled magnetization vs. temperature curves for all the samples with data taken in the cooling and warming cycles, LSPC3 showing significantly large hysteresis. The hysteresis loop is open since here the warming cycle is followed by the cooling cycle. C: The temperature dependence of magnetoresistance at 70 kOe for all the samples. D: The same at 5 kOe. The magnetoresistance is defined as  $\Delta\rho/\rho_0 = (\rho_H - \rho_0)/\rho_0$

(TMR)<sup>7,9</sup> and enhanced noise due to high junction resistance<sup>10</sup> or magnetic fluctuations<sup>11</sup>. In this respect, manganite multilayers can become a useful alternative in that they can be easily grown and do not necessarily need to be microfabricated. The resistance is much less compared to the MTJs and hence the noise level is low. Very recently, it was shown that the reduction in individual layer thickness in an all-ferromagnetic manganite multilayers can lead to giant enhancement of room temperature MR<sup>12</sup>, followed by observation of large room temperature MR in another all-ferromagnetic manganite superlattice<sup>13</sup>. On the other hand, there are several reports on ferromagnetic/antiferromagnetic manganite superlattice systems<sup>6,14–19</sup>. However, in all those cases, as will be discussed later on, the magnetoresistive response is either miniscule or confined within a very short temperature range away from room temperature. In this letter, we will also show that it is possible to achieve colossal magnetoresistive response over a wide temperature range even in ferromagnetic metal - antiferromagnetic charge-ordered insulator LSMO/PCMO multilayers.

Five multilayers have been prepared using pulsed laser ablation of  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  (LSMO) and  $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  (PCMO) ceramic targets, deposited on  $\text{SrTiO}_3$  substrates held at a temperature 800°C in 350 mTorr oxygen pressure. The prepared multilayers can be divided into two sets having different volume ra-

tio of LSMO and PCMO. The first set contains multilayers where the volume ratio of LSMO and PCMO is 1:1, while for the second set the volume ratio is 3:2. The detailed description of the different samples has been given in Table: I. The x-ray diffraction  $\theta - 2\theta$  scan plotted in Fig: 1D shows the (002) distinct superlattice reflections (Fig: 1D) for LSPC3. The sample diffraction peaks are as sharp as the substrate peak, indicating high structural quality. The calculated out-of-plane lattice parameters for LSMO and PCMO for the multilayers turn out to be 3.85 and 3.75 Å, respectively. These values being smaller than the corresponding bulk values 3.88 and 3.83 Å, respectively, confirms the highly epitaxial nature of the multilayers and the bi-axial in-plane tensile stress due to the substrate. The magnetotransport properties have been studied using the usual four probe method with the magnetic field applied parallel to the electric field.

In addition, as reference samples, transport properties of LSMO and PCMO films of thickness 500 Å deposited on STO substrates have been studied. The resistivities of both films show very weak sensitivity to magnetic field (Fig: 1A, B). It is obvious from Fig: 1A that even a magnetic field as high as 70 kOe is unable to destabilize, presumably, what should essentially be the charge-ordered state in PCMO. It is difficult to pinpoint the charge ordering transition from magnetization measurement due to extremely weak magnetic signal of the film superimposed on the large diamagnetic signal of the substrate. The charge ordering temperature can be ascertained from the temperature dependence of resistivity using the methodology employed in ref<sup>20</sup>, in which  $T_{co}$  can be determined from the plot of  $\log \rho$  against  $1/T$ , as shown in Fig. 1C. The plot shows three regimes where the high temperature and the low temperature regime is separated by a transition region within which  $\rho$  increases more strongly. In this case,  $T_{co}$  turns out to be 255 K, well above the  $T_{co} = 220\text{K}$  for the corresponding bulk sample<sup>21</sup>. This is consistent with previous results where enhancement of  $T_{co}$  due to bi-axial strain (compared to the bulk) was observed in films<sup>22</sup>. The critical magnetic field for charge-order melting in the corresponding bulk sample is about 60 kOe<sup>23</sup> while for the present case, the critical field seems to be beyond 70 kOe which is consistent with the enhanced value of  $T_{co}$ . The biaxial strain can influence two important parameters which determine the co-operative interaction and hence the transport or the magnetic properties: 1) The extension or contraction of the Mn-O-Mn bond-length leads to a large reduction or enhancement of the electronic hopping amplitude; 2) the increased Jahn-Teller distortion leads to localization of electrons. The experimental results for PCMO film described here are in agreement with already published report<sup>22</sup> and suggest that the bi-axial strain imposed by the substrate stabilizes the charge ordering in PCMO film.

The resistivity and the field cooled magnetization of all the samples in absence of magnetic field during the cooling and warming cycle has been plotted in Fig: 2A, B

TABLE I: Detailed description of the multilayers studied

Sample name	Description	$\rho_{5K}$ ( $\Omega cm$ )	$\rho_{300K}$ ( $\Omega cm$ )	$T_C$ (K)	$T_{MI}$ (K)
LSPC1	LSMO <sub>10Å</sub> /PCMO <sub>10Å</sub>	35.2	0.09	110	75
LSPC2	LSMO <sub>15Å</sub> /PCMO <sub>10Å</sub>	0.004	0.07	240	262
LSPC3	LSMO <sub>15Å</sub> /PCMO <sub>15Å</sub>	0.22	0.1	100	150
LSPC4	LSMO <sub>22.5Å</sub> /PCMO <sub>15Å</sub>	0.01	0.06	160	213
LSPC5	LSMO <sub>22.5Å</sub> /PCMO <sub>22.5Å</sub>	0.13	0.1	200	200

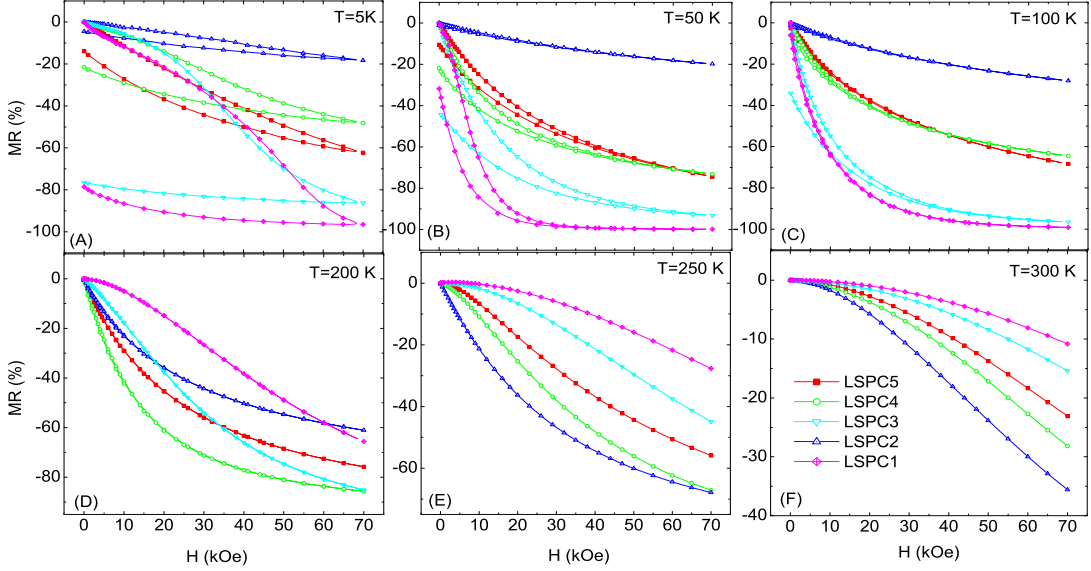


FIG. 3: (Color online) The magnetic field dependence of magnetoresistance for all the samples at different temperatures. All the multilayers exhibit varying degree of metastability at low temperature.

respectively. There are a few interesting points 1) Keeping the LSMO/PCMO volume ratio constant at 1 : 1, as the number of interfaces is increased, the low temperature resistivity increases significantly. 2) As the LSMO volume fraction is increased the temperature dependence of resistivity becomes distinctly metallic with high value of  $T_{MI}$ . Keeping the volume ratio constant, the increase in PCMO layer thickness leads to reduction in  $T_{MI}$  value. 3) Particularly for LSPC3, both the resistivity and the field-cooled magnetization curves during the cooling and warming cycle shows hysteresis.

Although the parent materials LSMO and PCMO hardly exhibit any significant MR within the temperature range 5 – 300 K, extra-ordinary enhancement of MR has been observed for all the multilayers (Fig: 2C, D and Fig: 3). LSPC1 and LSPC2 exhibits close to 100% MR (here the MR has been calculated using the so-called

pessimistic definition) over a wide temperature range and the magnetoresistance is quite large even at low magnetic field (Fig: 2D). As the thickness of the LSMO layer or the volume fraction of LSMO is further increased, large magnetoresistance is observed near room temperature.

The electronic conduction in manganites is governed by the competition between different energy scales such as the kinetic energy of the  $e_g$  electrons and the on-site Coulomb repulsion. If both energy scales become comparable, which is most likely for narrow bandwidth systems, there is a tendency towards phase separation into ferromagnetic metallic and anti-ferromagnetic charge-ordered insulating regions<sup>24</sup>. In this case, the phase coexistence has been introduced artificially by depositing alternate LSMO and PCMO layers of nanoscale thickness, and the magnetotransport properties observed mimic the properties exhibited by electronically phase-separated man-

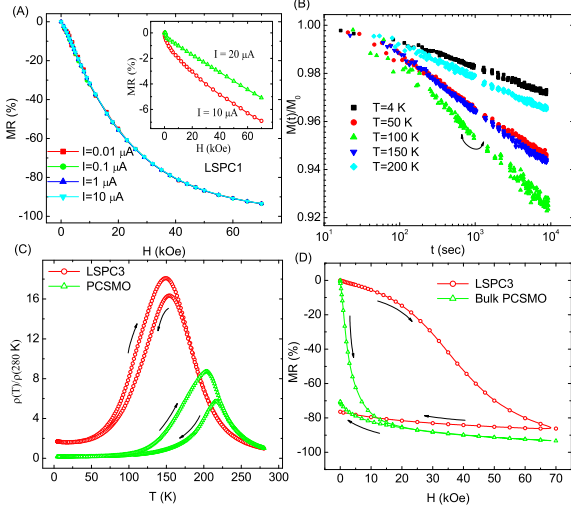


FIG. 4: (Color online) A) The bias dependence of MR (the bias dependence of MR of a granular NSMO film is shown in the inset for comparison) at 200 K for LSPC1. B) The magnetic relaxation data for LSPC3 at different temperatures C) The temperature dependence of resistivity and D) the magnetic field dependence of resistivity for LSPC3 and bulk PCSMO (for comparison) at 4 K showing signatures of metastability.

ganites, for example, metastability, long-time magnetic relaxation<sup>24</sup>, etc.

Fig: 3A gives strong evidence of metastability at low temperature in that the low-resistance-state obtained after the sample is exposed to strong magnetic field is retained even after the magnetic field is removed. The high resistance state is recovered when the temperature is raised to sufficiently high value and then zero-field cooled back to the low temperature. As the temperature is increased, due to thermal fluctuation, the width of the hysteresis curve gets reduced. The rate at which the magnetic field is swept, has been kept constant for all measurements. The temperature and magnetic field dependence of resistivity of a typical electronically phase-separated polycrystalline manganite sample  $\text{Pr}_{0.65}(\text{Ca}_{0.6}\text{Sr}_{0.4})_{0.35}\text{MnO}_3$  (PCSMO) has been compared with that for LSPC3 (Fig: 4D), showing similar evidence of metastability. This metastability has been directly verified from magnetic relaxation measurements carried out at different constant temperatures over the temperature range 4 – 250 K. A magnetic field of 50 kOe was applied for 60 sec after which the field was removed, followed by data collection over a time-span of 2 hours. The magnetic relaxation data shown in Fig: 4B corresponds to LSPC3. The long-time relaxation is clearly logarithmic and the negative slope-value of the reduced magnetization vs. time curves increases systematically as the temperature is decreased up to 100 K. Below 100 K, a completely opposite trend is observed (Fig: 4B).

The magnetic relaxation at long time scales can be described approximately by the expression  $M(t)/M(t_n) = 1 + S \log(t/t_n)$ . Here,  $S$  is called magnetic viscosity, and  $t_n$  and  $M(t_n)$  are the normalization time and the corresponding magnetization at that point in time, respectively. The logarithmic relaxation can be attributed to a free energy landscape containing local minima corresponding to different equilibrium states separated by energy barriers. Or to put it in another way, after the magnetic field is removed, the charge-ordered fraction tries to reappear at the expense of ferromagnetic fraction, resulting in long-time relaxation. At low temperature, after removing the magnetic field, the system gets trapped in a frozen cluster-glass like state due to the frustration at ferromagnetic (FM)/ antiferromagnetic (AFM) interfaces which relaxes extremely slowly with time, compared to higher intermediate temperature. Such long-time relaxation is only observed for LSPC1 and LSPC3, the rest of the samples do not exhibit any significant magnetic relaxation. Interestingly, so far as magnetotransport is concerned, the manifestation of metastability is more distinct in LSPC1 and LSPC3, compared to the other samples. As the thickness of the LSMO and PCMO layers is increased the observed metastability is comparatively less pronounced, suggesting the importance of the length scale of these inhomogeneities. Moreover, if the volume fraction of LSMO is increased compared to PCMO, the signatures of metastability get even weaker.

The highest value of MR at room temperature is about 36% (Fig: 3F), which is comparable to or better than that corresponding to all-ferromagnetic manganite multilayers reported so far<sup>12,13</sup>. The direct exchange coupling between FM/AFM layers due to the proximity of the ferromagnetic LSMO layers can induce an effective internal field<sup>14,25</sup>. The large value of MR observed in our case can be attributed to the lowering of critical magnetic field needed externally for melting of charge ordered state due to the introduction of ferromagnetic layers which can produce large internal magnetic field. In bulk PCMO samples, the ground state is a charge-ordered (CO) AFM phase<sup>23</sup>. However, for LSMO/PCMO or LCMO/PCMO multilayers, it has been observed that while the PCMO layers are still AFM, the CO state is not realized<sup>6,15,19</sup>. Due to the strong electron-phonon coupling, strain fields play a key role in the formation of CO phase. Thus the suppression of charge ordering in the above-mentioned experiments must be related with lattice strain and interface clamping<sup>6</sup>. Even in our case, since the critical magnetic field for melting of charge ordering in the PCMO film is distinctly higher compared to the bulk, the effect of strain fields cannot be ruled out.

All the multilayers show remarkable bias-stability at all temperature, over at least 4 orders of magnitude (Fig: 4A, B). This suggests that the multilayers are free from extrinsic effects such as spin dependent inter-granular transport<sup>26,27</sup>. The sharp bias dependence of MR for a granular  $\text{Nd}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  is shown in the inset of Fig: 4A, for comparison. The negligible bias dependence

of MR is ideally suited for application as magnetoresistive sensors. The fact that there is no hysteresis in the magnetic field dependence of MR above 100 K, adds to the prospect of the multilayers being qualified as potential magnetoresistive sensors. The resistivities of all the samples are reasonably low and epitaxial manganite films are known to exhibit extremely low  $1/f$  noise<sup>28</sup>.

As mentioned in the introduction, there are a few reports on all-manganite FM-metal/AFM-insulator superlattice systems<sup>6,14–19</sup>. While some of them deals with magnetic properties and exchange biasing effect at the FM-AFM interfaces<sup>6,14,16,18</sup>, in some cases, magnetotransport properties have also been studied. For example, large low field magnetoresistance (LFMR) has been observed in LCMO/PCMO superlattice<sup>15,19</sup>. However, in such cases there is hardly any evidence of the influence of charge ordering and the LFMR is observed round about the Curie temperature of LCMO and the enhancement of MR compared to the parent LCMO film (which is known to exhibit colossal MR anyway) is not substan-

tially high. In our case, the enhancement of MR has been observed over a large temperature range, without using colossal magnetoresistive material such as LCMO. Moreover, the magnetotransport properties give strong evidence of the influence of charge ordering, which can be easily destabilized using magnetic field, in complete contrast to the highly stable charge-ordered state in PCMO film described here and reported by other group<sup>22</sup>.

To conclude, colossal enhancement of MR has been achieved over a wide temperature range in LSMO/PCMO multilayers, rarely observed in any manganite multilayers till date. The colossal magnetoresistance has been attributed to the melting of charge-ordered state by magnetic field. There is no fundamental difference between the observed transport and magnetic properties of the multilayers (such as metastability and long-time relaxation) where the nanoscale phase separation has been introduced artificially and that of spontaneously phase-separated manganites.

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